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Inventor(s): Koichi Ashizawa et al

For: CURRENT COLLECTOR WITH PENETRATED HOLES OF COMPLICATED SHAPE
FOR USE IN SECONDARY BATTERY AND MANUFACTURING PROCESS
THEREOF

Enclosed are:

(X) 15 page(s) of specification (X) Abstract

() Executed Declaration/ (X) Inventors' Addresses
Power of Attorney

(X) 1 sheet(s) of (X) formal () informal drawings

() An Assignment of the application to _____

() Preliminary Amendment () Information
Disclosure Statement

() Associate Power of Attorney () Verified Statement Under
37 CFR 1.9 and 1.27

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Plant	XXXXXX	XXXXXX	\$530.00	\$265.00
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Priority is claimed under 35 USC 119 based on the following:

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Certified copy (copies) enclosed.

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Respectfully submitted,

By:



Felix J. D'Ambrosio
Reg. No. 25,721

ADDRESS: Jones, Tullar & Cooper, P.C.
P.O. Box 2266 Eads Station
Arlington, VA 22202

TELEPHONE: (703) 415-1500

INVENTORS' ADDRESSES

1. Koichi Ashizawa
61-8, Sasatani, Yamaderacho,
Kusatsu-shi,
Shiga, 525 Japan
2. Atsushi Mori
61-8, Sasatani, Yamaderacho,
Kusatsu-shi,
Shiga, 525 Japan

TITLE OF THE INVENTION

Current Collector with Penetrated Holes of Complicated Shape
for Use in Secondary Battery and Manufacturing Process Thereof

BACKGROUND OF THE INVENTION

5 1. Technical field of the invention

The present invention relates to a current collector for use in a secondary battery, particularly in a lithium secondary battery or lithium-ion battery, and to a manufacturing process thereof.

10 2. Prior arts

The secondary battery essentially comprises a positive electrode, a negative electrode, a separator for insulating the positive electrode and the negative electrode from each other, and an electrolyte for making it possible to move ion between 15 the positive electrode and the negative electrode. The positive electrode and the negative electrode are formed by coating the surface of a current collector of metal foil with an optional active material. For example, in the lithium ion battery, a current collector of aluminum foil coated with an active material 20 containing lithium cobaltate, etc. is used as a positive electrode, and a current collector of copper foil coated with an active material containing non-graphitizable carbon, etc. is used as a negative electrode.

Generally, there has been a problem that when coating a 25 surface of a metal foil such as aluminum foil or copper foil with

active material, the metal foil and the active material are difficult to be integrated or attached with each other, and the active material is relatively easy to drop out. In the preparation of a secondary battery, if a part of the active
5 material drops out at the time of winding the positive electrode and the negative electrode, there arises a problem of not being able to obtain a secondary battery of a desired capacity. If a part of the active material drops out after the preparation of the secondary battery, there arises another problem that charge
10 and discharge capacity of the secondary battery is gradually reduced.

To cope with this problem, it has been conventional to use a binder which in the active material has a good affinity with the metal foil. Further, it has been also conventional to use
15 a metal foil of which a surface has a good affinity with an optional binder. For example, the Japanese Laid-Open Patent Publication (unexamined) Hei 7-201332 discloses a technique in which an azole film such as benzotriazole is formed on a surface of a copper foil, thereby improving the integration between a binder of the
20 active material and the copper foil, and preventing the active material from dropping out.

On the other hand, being different from the mentioned method, another technique is also known, in which the active material is prevented from dropping out by forming penetrated
25 holes through the metal foil and integrating the active material

for coating front and back sides of the metal foil through these penetrated holes. It is certain that, in this method, as the active material, etc. on both sides are integrated through the penetrated holes, the active material, etc. are effectively
5 prevented from dropping out. But the adherence between each periphery or each inner wall of the penetrated holes and the active material, etc. or adherence between the metal foil and the active material, etc. still remains insufficient, and therefore if a large external force is applied, there is a possibility that a
10 part of the active material drops out.

SUMMARY OF THE INVENTION

The present invention intends to prevent effectively the active material from dropping out by improving the adherence between each periphery or each inner wall of the penetrated holes
15 and the active material, etc. To improve the adherence, the present invention adopts the following manner. That is, the active material is intruded to each periphery or each inner wall of the penetrated holes which are formed into a complicated shape (i.e., penetrated holes of complicated shape).

20 More specifically, the invention relates to a current collector provided with penetrated holes of complicated shape for use in a secondary battery, and to a manufacturing process thereof, characterized in that the current collector comprises a metal foil provided with a large number of penetrated holes,
25 and supposing that an area of a penetrated hole is S, a periphery

length of the penetrated hole is M, and a periphery length (= a circumference length) of a virtual circle having the area S of the penetrated hole is N, each penetrated hole satisfies the conditions of $0.05 \leq S \leq 50$ and $1.30 \leq M/N \leq 100$. The dimension of 5 S is mm^2 , and each dimension of M and N is mm .

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the invention, an aluminum foil, an aluminum alloy foil, a copper foil or a copper alloy foil is used as a metal foil forming the current collector. Generally in the lithium secondary 10 battery or lithium-ion battery, the aluminum foil or the aluminum alloy foil is used as a current collector for forming the positive electrode, while the copper foil or the copper alloy foil is used as a current collector for forming the negative electrode. In the invention, the current collector can be prepared by using 15 a metal foil other than aluminum foil or copper foil. Because in the secondary battery, a metal other than aluminum or copper is also used to form a metal foil. Thickness of the current collector may be in the range of 5 to 100 μm and is usually in the range of 8 to 30 μm . The current collector made of an aluminum 20 foil used in the lithium secondary battery or lithium-ion battery is preferably in the range of 10 to 30 μm , and the current collector of a copper foil is preferably in the range of 8 to 25 μm . As for the copper foil, both rolled copper foil (obtained by rolling method) and electrodeposited copper foil (obtained

by electrodepositing method) may be preferably used. The invention is featured by each penetrated hole which is provided through the current collector and has a specific shape. First of all, the area S of each penetrated hole is in the range of 5 0.05 to 50 mm². The area of the penetrated hole means an area occupied by each penetrated hole when the current collector is placed horizontally and seen from vertically above. Accordingly, the area S of a penetrated hole can be easily obtained by taking a microphotograph from vertically above and using such means as 10 visual image analysis of the photographed penetrated hole. If the area of the penetrated hole is smaller than 0.05 mm², the active material, binder, etc. are difficult to get into the penetrated hole, the active material, etc., are difficult to intrude to the periphery or inner wall of the penetrated hole, 15 the adherence between the current collector and the active material, etc. is lowered, and a part of the active material is easy to drop out, which is not desirable. If the area of the penetrated hole exceeds 50 mm², total area of the penetrated holes in the current collector becomes excessively large, mechanical 20 strength of the current collector is reduced, and there is a possibility that the current collector is fractured at the time of preparing the secondary battery by winding the current collector.

In the second place, supposing that a periphery length (= 25 a circumference length) of the penetrated hole is M, and a

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periphery length of a virtual circle having the area S of the penetrated hole is N, a value M/N is required to be in the range of 1.30 to 100. In this respect, the periphery length M can be easily obtained by taking a microphotograph of each penetrated 5 hole and measuring an actual size by means of visual image analysis. On the other hand, the periphery length N of the virtual circle can be obtained by measuring the area S of the penetrated hole, calculating a value r from an expression $S = \pi r^2$, and further calculating $2\pi r$ which is N. In the invention, 10 the value M/N must be in the range of 1.30 to 100. If the value M/N is smaller than 1.30, any complicated shape of the periphery of the penetrated hole cannot be achieved, the active material, etc. are difficult to be intruded to the periphery, the adherence between the end edge periphery and the active material, etc. 15 becomes insufficient, and a part of the active material is easy to drop out, which is not desirable. If the value M/N is larger than 100, the effect of prevention of dropping out of the active material is saturated and not improved any more.

The shape of the penetrated hole provided through the 20 current collector according to the invention is not a regular form such as circle, equilateral polygon, equilateral square, equilateral triangle, ellipse, etc. but an irregular form of complicated shape as shown in Figs. 1 and 2, for example. In the shape shown in Fig. 1, at the periphery of the penetrated hole, 25 there are several portions each forming a wedge shape and

intruding into the metal foil. The active material, etc. intrude to these portions, whereby the adherence between the periphery and the active material, etc. is improved. In another shape shown in Fig. 2, at the periphery of the penetrated hole, there are 5 indented portions, and the active material, etc. intrude to these indented portions, whereby the adherence between the periphery and the active material, etc. is improved. The shape of the penetrated holes in the invention is not limited to that shown in Figs. 1 and 2, and any other shape may be adopted as far as 10 the value M/N is in the range of 1.30 to 100, as a matter of course. When the M/N remains in the mentioned range, each periphery of the penetrated holes becomes a relatively complicated shape, and the adherence between the periphery and the active material, etc. is improved. It is to be noted that the current collector is 15 provided with a large number of such penetrated holes of complicated shape, and therefore a pitch between the penetrated holes which adjoin each other may be about 0.5 to 10 mm, and the density of the penetrated holes may be about 1 to 400 holes/cm².

The current collector for use in a secondary battery 20 according to the invention is useful as far as a large number of penetrated holes of complicated shape are provided, irrespective of the manufacturing method of the current collector. However, the following embossing method is most preferable as the manufacturing method. First, a metal foil 25 without hole such as copper foil without hole or aluminum foil

without hole is prepared. In this respect, "without hole" means that there is no penetrated hole having the mentioned area of 0.05 to 50 mm², and does not mean that there is no pinhole.

Accordingly, even if there is any pinhole of a very small diameter,

- 5 the metal foil having such a pinhole is classified into the metal foil without hole.

The metal foil without hole is caused to pass through between a concavo-convex roll having a large number of convex parts and a smoothing roll under a predetermined pressure. The 10 convex parts of the concavo-convex roll press the metal foil without hole, whereby the metal foil without hole is broken in the pressed points. The operation of such breakage is different depending on the pressure. For example, if the pressure is set to be relatively low, the breakage shows a condition that the 15 metal foil is torn off, and penetrated holes (of complicated shape) formed by tearing off the metal foil are obtained. That is, a penetrated hole as shown in Fig. 1 is obtained. On the other hand, if the pressure is set to be relatively high, the breakage shows a condition that the metal foil is punched, and penetrated 20 holes (of complicated shape) formed by punching the metal foil are obtained. That is, a penetrated hole as shown in Fig. 2 is obtained. Difference in the operation of breakage when setting the pressure to a certain value occurs depending on kind of the metal foil, material of the concavo-convex roll, material of the 25 smoothing roll, rotation speed of the concavo-convex roll and

the smoothing roll, and is not fixed.

Material of the concavo-convex roll is generally a metal, and that of the smoothing roll is generally an elastic roll such as rubber roll. As the smoothing roll is an elastic roll, the 5 convex parts of the concavo-convex roll can easily intrude in the elastic roll, and the metal foil without hole becomes easy to be provided with penetrated holes. A large number of convex parts are provided on the surface of the concavo-convex roll so that the metal foil without hole is provided with a large number 10 of penetrated holes. It is not always necessary that each top end of the convex parts is a complicated shape, but the top end may be a regular shape such as circle, square, triangle, polygon, etc. The top end of the convex parts may have any area, and is preferably in the range of about 0.05 to 50 mm².

15 By passing the metal foil without hole through between the concavo-convex roll and the smoothing roll, the metal foil without hole is converted into the metal foil with penetrated holes of complicated shape, and sometimes any burrs may be produced on the back side (i.e., on the surface where the metal 20 foil comes in contact with the smoothing roll) of the metal foil at each periphery of the penetrated holes. In particular, when the pressure between the concavo-convex roll and the smoothing roll is set to be relatively high, the burrs are easy to be produced. If there are any such burrs, the current collector for the positive 25 electrode and the collector for the negative electrode may

contact each other by passing through the separator and there is a possibility of short circuit in the secondary battery. Accordingly, the burrs may be left as they are when the extent of projection of the burrs is small, but are generally removed.

- 5 As a method for removing burrs, for example, the metal foil provided with the penetrated holes is caused to pass through between a pair of metal smoothing rolls. That is, as the pair of metal smoothing rolls press the metal foil provided with the penetrated holes at any pressure, burrs produced on each
10 periphery of the penetrated holes are forcibly pushed into the inner wall side of the periphery. As a result, burrs produced on each periphery of the penetrated holes are successfully removed.

In the mentioned manner, a current collector comprising
15 a metal foil provided with a large number of penetrated holes of relatively complicated shape is obtained. This current collector is preferably used as a current collector for a secondary battery such as lithium-ion battery, lithium metal battery, polymer battery, etc. The current collector is also
20 preferably used as a current collector for a secondary battery other than the lithium secondary battery.

In the current collector for a secondary battery comprising a metal foil provided with a large number of penetrated holes according to the invention, since each periphery of the
25 penetrated holes has a complicated shape, the active material,

binder, etc. coating both sides of the current collector intrude to each periphery or each inner wall of the penetrated holes, and the active material, etc. on both sides are integrated.

Accordingly, an advantage is performed such that the adherence
5 between the active material, etc., and each periphery of the
penetrated holes is improved, and the active material, etc.
applied to both sides of the current collector are difficult to
drop out.

As a result, at the time of winding the current collector
10 (for the negative or positive electrode used in the secondary
battery) coated with the active material, etc. and preparing a
secondary battery, a further advantage is performed such that
the active material, etc. drop out little, and a secondary battery
having a desired capacity can be easily prepared. Furthermore,
15 after preparing the secondary battery, the drop out of the active
material, etc. or the separation of the active material, etc.
and the current collector from each other can be successfully
prevented, whereby the reduction in the charge and discharge
capacity is prevented and a life of the secondary battery is
20 prolonged.

The current collector according to the invention can be
easily and reasonably obtained just by passing the metal foil
without hole through between the concavo-convex roll and the
smoothing roll. By further passing through between a pair of
25 metal smoothing rolls after passing through between the

concavo-convex roll and the smoothing roll, even if any burrs are produced on each periphery edge of the penetrated holes, the burrs can be easily and reasonably removed. Consequently, by adopting the above-described method, the current collector according to the invention can be efficiently obtained at a relatively low cost.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an enlarged view of a surface of a current collector according to an example of the invention, showing schematically a shape of a penetrated hole.

Fig. 2 is also an enlarged view of a surface of a current collector according to an example of the invention, showing schematically a shape of another penetrated hole.

EXAMPLES

Several examples of the invention are hereinafter described, but the invention is not limited to those examples. The invention should be understood or interpreted based on the idea that, as each periphery of a large number of penetrated holes provided through a current collector is formed into a specific complicated shape, the active material, etc. coating both ends of the current collector intrude to each periphery or each inner wall of the penetrated holes and become difficult to drop out.

EXAMPLE 1

First, a rolled copper foil without hole of 25 cm in width 25 300 m in length and 18 μ m in thickness was prepared. This rolled

copper foil was caused to pass through between a later-described concavo-convex roll and a smoothing roll at a feed speed of 20 m/min under a pressure of 7.5 kgf/mm. The mentioned concavo-convex roll has convex parts each of which adjoin each other at 5 a pitch of 5 mm in both cross direction and length direction, and a top end of each convex part is formed into a circle having a diameter of 0.8 mm. This concavo-convex roll is made of a metal, and its roll diameter is 200 mm and its roll width is 300 mm. On the other hand, the smoothing roll is made of a rubber roll 10 of which surface is coated with NBR (Neobutadiene Rubber), and its roll diameter is 250 mm and its width is 300 mm.

As a result, the rolled copper foil without hole was provided with penetrated holes at the points corresponding to the convex parts of the concavo-convex roll. Each shape of the 15 penetrated holes was similar to that shown in Fig. 1. Then, as a result of measuring and calculating an area S of each penetrated hole, a periphery length M of the penetrated hole, and a periphery length N of a virtual circle having the area S, it was found that $S = 0.50 \text{ mm}^2$ and $M/N = 2.5$. When coating both sides of this current 20 collector with a mixture of an active material comprising a non-graphitizable carbon and a fluoride binder, drop out of the active material was little, and a current collector preferably used as a negative electrode of a lithium-ion secondary battery was obtained.

In the same manner as Example 1, except that the pressure between the concavo-convex roll and the smoothing roll was 20 kg/mm, a copper foil provided with penetrated holes at the points corresponding to the convex parts of the concavo-convex roll was obtained. Each shape of the penetrated holes was similar to that shown in Fig. 2, and relatively large burrs were formed on the back side of the copper foil (i.e., on the surface of the copper foil in contact with the smoothing roll) at each periphery of the penetrated holes. The copper foil with the penetrated holes was caused to pass through between a pair of metal smoothing rolls (of which each roll diameter was 250 mm and roll width was 300 mm) under a pressure of 4.4 kgf/mm at a feed speed of 20 m/min.

As a result, burrs formed on the back side of the copper foil at each periphery of the penetrated holes were almost removed. In the same manner as Example 1, S, M and N were measured and calculated, and it was found that $S = 0.50 \text{ mm}^2$ and $M/N = 3.5$. When coating both sides of this current collector with a mixture of an active material comprising a non-graphitizable carbon and a fluoride binder, drop out of the active material was little, and a current collector preferably used as a negative electrode of a lithium-ion secondary battery was obtained.

COMPARATIVE EXAMPLES 1 TO 4

The same rolled copper foil as used in Example 1 was provided with a large number of circular penetrated holes of 0.50 mm^2 in area by punching, and a current collector was obtained

(Comparative Example 1). In the same manner, current collectors respectively provided with a large number of equilateral polygonal penetrated holes (Comparative Example 2),
equilateral square penetrated holes (Comparative Example 3), and
5 equilateral triangular penetrated holes (Comparative Example 4) were obtained. In case of the circular penetrated holes, M/N was 1.00; in case of the equilateral polygonal penetrated holes, M/N was 1.05; in case of the equilateral square penetrated holes, M/N was 1.13; and in case of the equilateral triangular penetrated
10 holes, M/N was 1.29.

When coating each both sides of these four kinds of current collectors with a mixture of an active material comprising a non-graphitizable carbon and a fluoride binder, drop out of the active material was much as compared with Examples 1 and 2.

What is claimed is:

1. A current collector for use in a secondary battery consisting of a metal foil provided with a large number of penetrated holes, each of which has a complicated shape and
5 satisfies the following expressions (1) and (2):

$$0.05 \leq S \leq 50 \quad \dots \quad (1)$$

$$1.30 \leq M/N \leq 100 \quad \dots \quad (2)$$

[where: S is an area (mm^2) of the penetrated hole, M is a periphery length (mm) of the penetrated hole, and N is a periphery length
10 (mm) of a virtual circle having the area S of the penetrated hole.]

2. A current collector for use in a secondary battery according to claim 1, wherein thickness of the metal foil is in the range of 5 to 100 μm .

3. A method for producing a current collector for use in
15 a secondary battery according to claim 1, wherein by passing a metal foil without hole through between a concavo-convex roll having a large number of convex parts and a smoothing roll under a certain pressure, portions of the metal foil without hole pressed by the convex parts of said concavo-convex roll are
20 converted into penetrated holes.

4. A method for producing a current collector for use in
a secondary battery according to claim 1, wherein after
converting the portions of a metal foil without hole into
penetrated holes by passing the metal foil without hole through
25 between a concavo-convex roll having a large number of convex

parts and a smoothing roll under a certain pressure, the metal foil with the penetrated holes is caused to pass further through between a pair of metal smoothing rolls, whereby burrs produced at each periphery of the penetrated holes are removed.

ABSTRACT OF THE DISCLOSURE

There is provided a current collector for use in a secondary battery on which active material coating both sides of a metal foil are difficult to drop out.

- 5 The metal foil is provided with a large number of penetrated holes, periphery of the penetrated holes is formed into a complicated shape, and active material, binder, etc. are intruded to each periphery, whereby the active material, etc. coating both sides of the current collector consisting of the metal foil are
10 10 prevented from dropping out. An area S of the penetrated holes is in the range of 0.05 to 0.50 mm². Supposing that a periphery length of the penetrated hole is M, and a periphery length of a virtual circle having the area S of the penetrated hole is N, a value M/N is in the range of 1.30 to 100. The current collector
15 15 having such a large number of penetrated holes is obtained by passing a metal foil without hole through between a concavo-convex roll having a large number of convex parts and a smoothing roll. If any burr is produced at each periphery edge of the penetrated holes, the current collector is further caused to pass
20 20 through between a pair of metal smoothing rolls, whereby the burr produced on each periphery edge of the penetrated holes can be removed.

Fig. 1

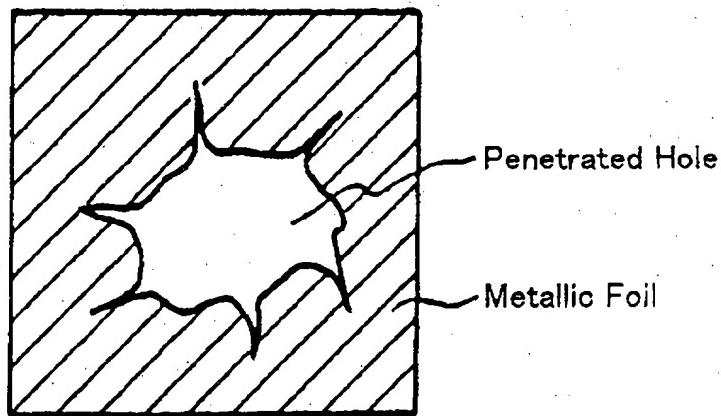
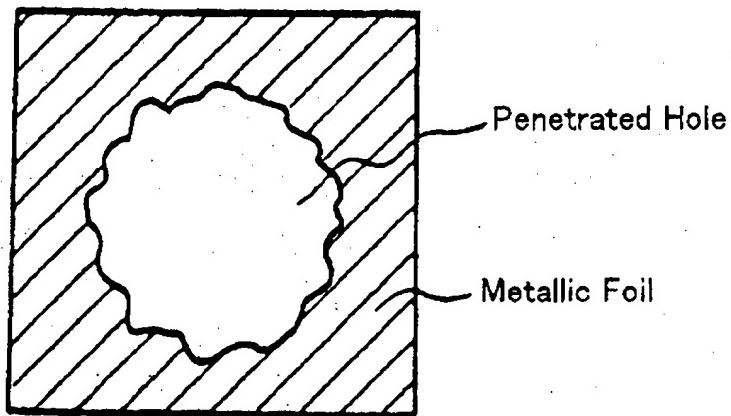
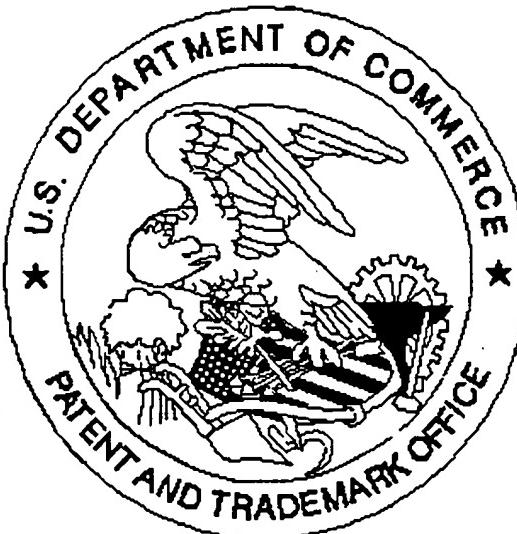


Fig. 2



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